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Assembly of a tri-silver metallo-capsule incorporating a tripodal tris-pyridyl ligand

David J. Bray,^a Li-Ling Liao,^b Bianca Antonioli,^c Karsten Gloe,^c Leonard F. Lindoy,^{*a} John C. McMurtrie,^a Gang Wei^{*d} and Xiao-Yi Zhang^{*b}

- ^a Centre for Heavy Metals Research, School of Chemistry, University of Sydney, NSW 2006, Australia. E-mail: Lindoy@chem.usyd.edu.au; Fax: +61 2 9351 3329; Tel: +61 2 9351 4400
- ^b School of Physics and Chemistry, Guizhou Normal University, Guiyang, Guizhou 550001,

P. R. China

- ^c Institut für Anorganische Chemie der TU Dresden, D-01062 Dresden, Germany
- ^d CSIRO, Industrial Physics, PO Box 218, Lindfield, NSW 2070, Australia

Received 15th April 2005, Accepted 3rd May 2005 First published as an Advance Article on the web 13th May 2005

A trinuclear metallo-capsule has been assembled from a new tripodal pyridyl ligand and three silver(I) ions; the Xray structure shows the presence of a Ag–Ag interaction in the solid state giving rise to a non-symmetric capsule arrangement while NMR evidence indicates that the structure in solution is symmetrical.

A frequent objective of metallo-supramolecular chemistry over the past few decades has been the design of ligands which can be directed, with the aid of a suitable metal ion, to form pre-determined architectures.¹ Prior research in this area has focussed on the use of a range of metal ions largely displaying four or six coordination geometries. In contrast, the use of two or three coordinate metal ions as structural components has been less exploited.²



We now report the synthesis of a molecular capsule which assembles from two flexible, potentially tripodal pyridyl ligands of type 1 and three silver ions to yield a colourless complex of stoichiometry $Ag_3L_2(NO_3)_3$ (L = 1). Ligand 1 was synthesised in 90% yield via a nucleophilic reaction between 4-mercaptopyridine and 1,3,5-tris(bromomethyl)benzene† that was based on a literature synthesis for related compounds.³ Addition of a methanol/acetonitrile solution of silver nitrate to a solution of 1 in methanol resulted in immediate precipitation of a white solid whose microanalysis showed it to be of stoichiometry $Ag_3L_2(NO_3)_3$. The positive ion mass spectrum (HR-ESI) of this complex yielded a peak corresponding to $[Ag_3L_3(NO_3)_2]^+$ with a ¹⁰⁷Ag, ¹⁰⁹Ag isotopic pattern that matched that calculated for this ion (Fig. 1); other peaks corresponding to $[Ag_2L_2(NO_3)]^+$, $[AgL_2]^+$ and $[AgL]^+$ were also present. The ¹H NMR spectrum of the product indicated that it had a highly symmetric structure in CD₃CN, indicative of the presence of equivalent silver sites in this solvent.

The X-ray structure of **2** (Fig. 2), recrystallised from acetonitrile, shows that each of the silver ions acts as a bridge between pairs of pyridyl groups on different ligands to produce the capsule-like structure illustrated in Fig. 2.§ Two of the silver









Fig. 2 The molecular structure of $[Ag_3(1)_2(NO_3)_2](NO_3)$. Two of the silver atoms are involved in a direct contact (distance 3.1621(4) Å). These two silver atoms are connected to the third *via* bridging nitrato oxygen atoms. The third nitrate counter ion does not coordinate to the metal complex.

ions are equivalent and interact *via* a Ag–Ag contact at 3.1621(4) Å; the latter separation is considerably less than the van der Waals diameter for silver (3.44 Å).⁴ Related Ag–Ag contacts in other systems have now been well documented.⁵ In the present structure, the two interacting silver centres are connected to the third centre by means of bridging nitrato groups

Inspection of molecular (CPK) models suggested that the binding of silver to the pyridyl rings of **1** rather than to its softer sulfur groups appears largely as a consequence of steric factors inhibiting the formation of a reasonable coordination geometry that involves the participation of all three sulfur donors of each ligand. In any case, a number of pyridyl-containing ligands have been documented previously^{7,8} to exhibit strong affinities for silver(I).

In an extension of the above study, competitive mixed metal, bulk membrane transport experiments (water/chloroform/ water) were also undertaken using **1** as the ionophore at

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 10^{-3} mol dm⁻³ in the chloroform phase. Details of the experimental arrangement and conditions employed have been described in more detail elsewhere.⁶ The aqueous source phase contained an equimolar mixture of cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II), silver(I) and lead(II) nitrate (each at 10^{-2} mol dm⁻³). The source and receiving phases were buffered at pH 4.9 and 3.0, respectively, and the metal concentration in the aqueous receiving phase was determined on termination of each experiment after 24 h. Under the conditions employed, clear transport selectivity for silver(I) occurred. Namely, silver was transported at a rate (*J*) of 178×10^{-7} mol per 24 h while no transport of any of the other six metals present in the source phase was observed within the detection limits of the experiments.¶

In conclusion, the interaction of silver(I) with the tripodal ligand 1 provides a facile means of generating a new trinuclear metallo-capsule. While the latter adopts a symmetrical structure in solution, a less symmetrical arrangement incorporating a Ag^{I} - Ag^{I} interaction between two of its three silver centres, is obtained in the crystalline state.

Acknowledgements

We thank Guizhou Normal University, the Deutsche Forschungsgemeinschaft and the Australian Research Council for financial support.

Notes and references

† Preparation of 1,3,5-tris((pyridin-4-ylthio)methyl)benzene (1). A suspension of 4-mercaptopyridine (15 mmol, 1.67 g), 1,3,5-tris(bromomethyl)benzene⁹ (5 mmol, 1.78 g) and triethylamine (20 mmol, 2.0 g) in acetonitrile (30 ml) was stirred at 0 °C for 18 h. The resulting solid was filtered, washed with water, and recrystallised from methanol/water resulting in a pale yellow solid (2.0 g, 90%). ¹H NMR (CDCl₃, 200 MHz, 300 K), δ : 4.17 (s, 6H, CH₂), 7.07 (d, 6H, py), 7.33 (s, 3H, C₆H₃), 8.36 (d, 6H, py). ¹³C NMR (CDCl₃, 75 MHz, 300 K), 35.77, 121.35, 128.78, 137.48, 149.02, 149.53. MS (ESI) *m/z* = 448.1 (M + H)⁺. Found: C, 64.15; H, 5.02; N, 9.08. C₂₄H₂₁N₃S₃ requires: C, 64.42; H, 4.73; N, 9.40%.

[‡] Preparation of $[Ag_3L_2(NO_3)_2]NO_3$ (L = 1). A solution of AgNO_3 (0.09 g, 0.5 mmol) in 15 ml methanol/acetonitrile (2 : 1) was added to a warm solution of 1,3,5-tris((pyridin-4-ylthio)methyl)benzene (0.22 g, 0.5 mmol) in MeOH (10 ml). This resulted in formation of the complex (0.15 g, 65%) as a white precipitate. Found: C, 41.39; H, 3.04; N, 8.99. C₄₈H₄₂Ag_3N₉O₉S₆ requires: C, 41.11; H, 3.02; N, 9.00%. HRMS-ESI (methanol) found 1342.8721. C₄₈H₄₂Ag_3N₈O₆S₆ requires 1342.8700, [Ag_3L_2(NO_3)_2]^{+.1}H NMR (acetonitrile-d₃, 200 MHz, 300 K), δ : 4.29 (s, 6H, CH₂), 7.19 (d, 6H, py), 7.46 (s, 3H, C₆H₃), 8.32 (d, 6H, py). This product was recrystallised from acetonitrile to yield crystals suitable for X-ray structure analysis. The complex is stable under ambient light conditions for months, with no noticeable coloration of the bulk sample when exposed to direct sunlight.

§ Full sphere data were collected at 150(2) K with ω scans to approximately 56° 2θ using a Bruker SMART 1000 diffractometer employing graphite-monochromated Mo-Kα radiation generated from a sealed tube (0.71073 Å). Data integration and reduction were undertaken with SAINT and XPREP¹⁰ and subsequent computations were carried out using the WinGX-32¹¹ graphical user interface. Multi-scan empirical absorption correction¹² was applied to the data using the program SADABS.¹³ The structure was solved by direct methods using SIR97¹⁴ then refined and extended with SHELXL-97.¹⁵ Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealised positions and refined using a riding model. The refinement residuals are defined as $RI = \Sigma ||F_o|| - |F_c||/\Sigma |F_o||$ for $F_o > 2\sigma(F_o)$ and $wR2 = {\Sigma [w(F_o^2 - F_c^2)^2]/\Sigma [w(F_c^2)^2]}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0362P)^2 + 2.2743P]$, $P = (F_o^2 + 2F_c^2)/3$. Crystal data: $[Ag_3(1)_2(NO_3)_2]NO_3$; Formula $C_{48}H_{42}Ag_3N_9O_8G_o$, M = 1404.88, monoclinic, space group $P2_1/n$ (#14), a = 14.4759(14) Å, b = 16.4153(16) Å, c = 22.157(2) Å, $\beta = 90.879(2)^\circ$, V = 5264.5(9) Å³, $D_c = 1.773$ g cm⁻³, Z = 4, crystal size 0.28 × 0.23 × 0.17 mm, colourless, habit columnar, temperature 150(2) K, λ (Mo-K α) = 0.71073, μ (Mo-K α) 1.407 mm⁻¹, T(Empirical)_{min,max} = 0.713, 0.787, $2\theta_{max} = 56.62$, hkl range -18 to 18, -20 to 21, -29 to 28, N = 51185, $N_{ind} = 12583$ ($R_{merge} = 0.0461$), $N_{obs} = 9153$ ($I > 2\sigma(I)$), $N_{var} = 676$, residuals $R1(F, 2\sigma) = 0.0364$, $wR2(F^2, all) = 0.0822$, GoF(all) = 1.011, $\Delta\rho_{min,max} = -0.516$, 1.024 e Å⁻³. CCDC reference number 265029. See http://www.rsc.org/supdata/dt/b5/b503565j/for crystallographic data in CIF or other electronic format.

 $\P A J$ value of 20×10^{-7} mol per 24 h corresponds to the detection limit for the transport runs and any apparently smaller values were treated as zero.

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